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PITTSBURGH ATMOSPHERIC SCIENCES INSTITUTE

TECHNICAL PROGRESS SUMMARY NO. 11

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NAME OF CONTRACTOR:

Departments of Physics and Chemistry
University of Pittsburgh
Pittsburgh, Pennsylvania 15213

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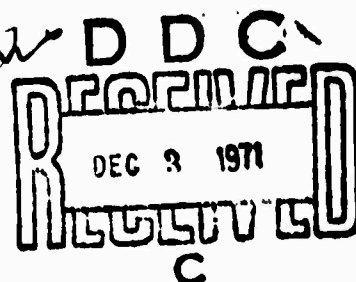EXPIRATION DATE:

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PROJECT SCIENTIST:

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TITLE OF WORK:

ATOMIC AND MOLECULAR PROCESSES
IN ATMOSPHERIC ENVIRONMENTS

October 28, 1971

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I. Summary of Research

The following research projects are identified by title,
senior investigator(s) in charge of the work, and task designation(s)
in the ARPA work statement. This summary only covers advances during the
period since our last progress report (dated April 28, 1971).

A. Laboratory Studies

1a. Radiative Properties of Simple Molecules for Optical Discrimination
Studies (F. Kaufman) (Tasks a and d).

A large number of experiments were performed with modulated or steady
excitation of SO_2 to its excited singlet ($^1B_1$) at incident wavelengths
of 2800, 2900, 3000, 3100, and 3170Å, at about 25Å full width at half
maximum Lifetimes and quenching constants were measured at SO_2
pressures from 0.5 to about 30 millitorr which permits extrapolation
to zero pressure and determination of the radiative lifetime. The
radiative lifetime appears to decrease from more than 100 µsec
at 2800Å to about 25 µsec at 3170Å excitation. Neither the $1/\tau$ vs.
p plots nor the p/I vs. p (Stern-Volmer) plots are linear, indicating
that both vibrational and electronic energy transfer processes are
occurring and that possibly more than one electronically excited
state may be populated in the initial absorption process. This would
be in some conflict with the presently available spectroscopic

information and will be checked carefully. From the slopes of the $1/\tau$ vs. p plots it appears that quenching processes are very efficient, nearly gas kinetic, and that stepwise vibrational relaxation in the electronically excited state is important, as had been found earlier to be the case for NO_2.

1b. **Radiative Properties of Simple Atoms and Molecules for Optical Discrimination Studies (E. C. Zipf) (Tasks a and d).**

Substantial progress has been made during this report period on several electron scattering experiments. These results are summarized below. The Werner band measurements are particularly important because they permit the molecular branching-ratio technique to be used in absolute VUV calibration work at wavelengths as short as $1100\overset{o}{A}$. A paper describing this work has been submitted to The Physical Review. In this paper we also describe the first successful observation of a rotational-intensity perturbation predicted on quantum mechanical grounds by Julienne. We have continued with our studies of electron impact on reactive atomic species such as N and O and we have been able to evaluate the importance of atomic nitrogen as a source of airglow and auroral emission features. We have also made a detailed study of electron-impact excitation of NO. These studies were prompted by our auroral mass spectrometer observations and a paper describing this work has been submitted to the Journal of Chemical Physics.

(a) Electron Impact Excitation of the Werner Bands of H_2.
The Werner band system of molecular hydrogen ($C\,^1\Pi_u \rightarrow X\,^1\Sigma_g^+$) was excited by electron impact on H_2 and studied in the wavelength region $1100\overset{o}{A} - 1250\overset{o}{A}$ with sufficient instrumental resolution to resolve much of the rotational

structure of the bands. The absolute cross section for the excitation of the Q1 line of each of the prominent bands in this wavelength region was determined. The absolute spectral sensitivity of the apparatus was determined by observing the dissociative excitation of Lyman-Alpha in H_2 and Lyman-band fluorescence in HD. It was found that the Werner bands are a satisfactory basis for a spectral sensitivity determination only if the intensity measurements are made with sufficient resolution (FWHM $\leq$ 0.44). The perturbation interaction between the B and C states of the hydrogen molecule was clearly observed in the rotational intensity distribution in one set of bands; these results will be discussed in detail.

(b) Electron Impact Excitation of Atomic Nitrogen. The absolute cross sections for the excitation of five NI vacuum-ultra-violet multiplets by electron impact on atomic nitrogen were measured from threshold to 350 eV. The following results were obtained:

Multiplets	$\lambda(\overset{o}{A})$	Q(max; cm^2)	E(max; eV)
$NI(3s^2P \rightarrow 2p^3\,^2P)$	1743	$1.8 \times 10(-17)$	17
$NI(3s^2D \rightarrow 2p^3\,^2D)$	1243	$1.7 \times 10(-17)$	17
$NI(3s^4P \rightarrow 2p^3\,^4S)$	1200	$5.5 \times 10(-16)$	25
$NI(3d^2D \rightarrow 2p^3\,^2D)$	1164	$4.0 \times 10(-17)$	18
$NI(2p^4\,^4P \rightarrow 2p^3\,^4S)$	1134	$4.8 \times 10(-16)$	22

The use of VUV absorption techniques to measure the absolute nitrogen density provided an opportunity to measure the oscillator strength of the $NI(2p^4\,^4P - 2p^3\,^4S)$ transition. The branching ratio for the $NI(\lambda 1164\overset{o}{A}/\lambda 1311\overset{o}{A})$ multiplets

was also determined. These results will be discussed in detail.

(c) Electron-Impact Excitation of Atomic Nitrogen in the Terrestrial Airglow. The absolute cross sections for the excitation of NI transitions in the vacuum ultra-violet due to the impact of low-energy electrons on atomic nitrogen have been measured in the laboratory. The cross sections for the resonance transitions at 1134Å and 1200Å are quite large [$Q(max) \sim 5 \times 10^{-16} cm^2$] while the excitation cross sections for other NI transitions in the VUV are comparatively small. When the absolute cross sections for the direct excitation of N are compared with the corresponding cross sections for dissociative excitation of N_2, striking differences in shape and magnitude are found to exist. In principal, these differences permit one to estimate the density of atomic nitrogen in the upper at-mosphere from an examination of VUV spectra obtained by satellites and sounding rockets. All data published up to the present indicate that the observed NI emissions in the day airglow and aurora are predominantly molecular in origin, and imply very low atomic nitrogen densities above 140 km.

(d) Electron-Impact Excitation of Nitric Oxide. The absolute cross sections for the excitation of the NO^+ Baer-Miescher bands ($A\,^1\Pi_u \rightarrow X\,^1\Sigma_g^+$), two nitric oxide β' bands ($\beta'\,^2\Delta_i \rightarrow X^2\Pi_r$), and several atomic nitrogen multiplets in the vacuum ultra-violet by electron impact on NO have been measured over an

energy range extending from threshold to 300 eV. The
variation of the dipole transition moment for the NO^+
$(A^1\Pi_u \rightarrow X^1\Sigma_g^+)$ band system was also determined.

2.   Clean Air Chemistry and Chemiluminescence (F. Kaufman) (Tasks a and d).
(a) In order to obtain strictly comparable values for the O + NO
radiative rate constant as function of pressure and wavelength, the
OI resonance light source (He plus trace O_2 discharge) and detector
(NO photoionisation) were extensively calibrated by producing known
concentrations of O in the flow tube from excess N with a small,
measured flow of added NO and comparing the experimentally observed
absorption with a computer calculation. In this calculation Doppler-
shaped lines of the emitted triplet, whose intensity ratios range
from 5:3:1 for negligible optical depth in the source to lower ratios
consirtent with any given optical depth, are absorbed by the three
J-states of atomic oxygen in thermal equilibrium in the large flow
tube. In this manner, a given O-concentration (measured by N + NO)
and measured light absorption (integrated over the triplet) uniquely
determines the extent of source "broadening", i.e. the O-concentration
in the source. It is this latter parameter which is quite variable
and almost impossible to set experimentally with any degree of
reliability, probably because of slight oxygen evolution from the glass
walls in the discharge region. The problem is thus subverted by
calibrating the light source/absorption system immediately before and
after each experiment in the above manner. An extensive, new series
of radiative rate constant measurements at pressures from 0.5 to 100
millitorr and wavelengths from 4000 to 7800Å were carried out, and
were properly corrected for source broadening. They show the predicted

decrease of the pseudo-bimolecular rate constant, I_o from the higher to the lower pressures, and they also show that the ratio I_o^{high}/ I_o^{low} decreases sharply from about 6 at and above 6000Å to about 1.5 at 4050Å. This arises from the fact that 4050Å is close to the high energy threshold of the chemiluminescence (~3975Å) so that virtually every collision which results in some vibrational relaxation (and these occur with roughly gas-kinetic cross section) removes the emitting NO_2^e, i.e. the emitters at the wavelength are mainly unstabilized collision complexes, whereas at longer wavelengths they include many, partially vibrationally relaxed NO_2^e molecules. The recent experiments bear out very nicely the correctness of our general mechanism. Miss Cody has completed all necessary experiments and most of her Ph.D. dissertation which she is expected to defend within one to two months.

(b) The completed experimental study of the important $0 + O_3 \rightarrow 2O_2$ reaction was fully analyzed and written up as a Ph.D. dissertation by Mr. McCrumb. The best least squares computer fit to all data points from 296 to 409°K gave an Arrhenius expression of 1.78×10^{-11} $\exp (-4.46kcal/RT)$ $cm^3 sec^{-1}$, slightly different from the earlier expression which was based on a graphical fit. Mr. McCrumb successfully passed his Ph.D. final examination and is now preparing a condensed version of his work for publication in the Journal of Chemical Physics.

The flow apparatus has been substantially modified by Dr. J. G. Anderson for the study of OH reactions of stratospheric and mesospheric importance such as $OH + O_3$, $OH + NO_2 + M$, $OH + NO + M$, etc. This is accomplished by placing a fixed fluorescence cell downstream of the heated or cooled reaction section and adding the stable reactant

(NO_2 or O_3) through a movable inlet tube. Excellent sensitivity and dynamic range have been achieved for the OH density measurement, and the desired reaction rates will soon be measured.

3. **Energy Partitioning in Metal Atom Chemi-Excitation (M.A. Biondi and F. Kaufman)**

    A new experimental system was designed and built for the study of the translational energy release in sodium atom excitation reactions by means of line shape studies using a Fabry-Perot interferometer. Much difficulty was encountered with a commercial, piezo-electric scanning interferometer which did not meet specifications in various ways and several of whose components had to be returned for repair or replacement. An overall finesse of 20 to 25 was finally obtained with good reproducibility, but the stability and drift problem is not yet fully under control. Experiments could be performed successfully for two systems, Na + Cl_2 and Na + "active nitrogen". The latter is the more important, because it has direct bearing on the question of energy transfer from vibrationally excited N_2 to Na. It is also experimentally easier to study, since sufficiently bright light emission is observed at Na temperatures as low as 180°C (where the optical depths is reasonably low) whereas the Na + Cl_2 glow is until now observed only above about 280°C. A computer program was developed which generates Doppler-shaped Na line profiles (including hyperfine structure) as function of temperature, and folds in the desired experimental finesse. Preliminary results for the Na + N system indicate a normal (unreversed) line-shape and a relatively low translational temperature ($\leq$ 1000°K). It has not yet been determined whether the excitation is due to N-atoms, i.e. to the highly excited N_2 species

formed early in the recombination, or to N_2^V from the discharge at more moderate excitation energies (~2 eV, near V=8 or 9). The N_2 discharge flow line has a titration inlet upstream of the emission cell, and in future experiments it will be possible to add "titrant" species such as NO, which removes N and produces N_2^V , or CO_2, which relaxes N_2^V but does not react with N, in order to clarify the precursor species in this energy transfer.

4. **Neutral-Neutral Reactions in Crossed Beams (W.L. Fite) (Tasks a and d).**

The crossed beam studies of the reaction Ba + O_2 has proceeded well during the past six months. Signal quality has improved and a very satisfactory curve of angular distribution of BaO has at last been obtained. Estimates of the reaction cross section have increased slightly, to a few times $10^{-16} cm^2$. Phase spectrometry measurements, used to determine the mean velocity of the reaction products have been confusing. Although the data appears reasonably satisfactory, we have not been able to reconcile in detail the data with any of the standard simple models of the reaction dynamics. Of particular concern is the fact that at some laboratory angles, the signal phases as a function of modulation frequency suggest that the reaction products emitted transversely to the line of centers of the reactants in center-of-mass coordinates have a total kinetic energy of about 0.3 eV (therefore, leaving about 0.3 eV in internal energy in the BaO), but that at other angles the division of energy between kinetic and internal energy changes.

Variation of temperature of the Ba did not reveal discernible changes in apparent rate coefficients, which permits the estimate that cross section for the triplet Barium metastable atom's reaction

cross section is not more than about one order of magnitude greater than the groundstate Barium atom's.

Attempts are currently being made to obtain a better absolute value for the groundstate atom's reaction cross section.

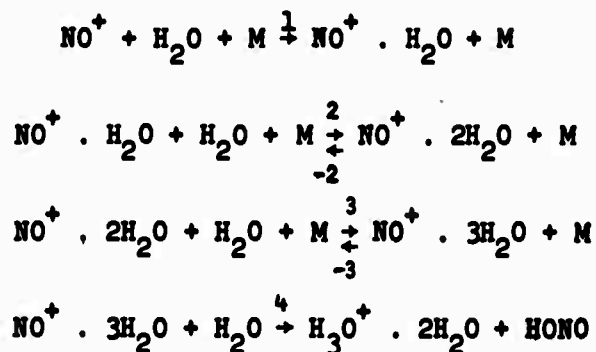5. **Processes Involving Metastable Species (E.C. Zipf) (Tasks c and d).**

We have continued with our studies of argon atoms in the metastable $Ar(^3P_{0,2})$ state with special emphasis on airglow and auroral applications. This work has yielded a number of interesting results which are summarized below:

(a) Collisional Deactivation of Metastable $Ar(^3P_{0,2})$ Atoms and $N_2(A^3\Sigma_u^+)$ Molecules. In a series of afterglow experiments, we measured the rate coefficients for the collisional depopulation of argon atoms in the metastable $^3P_{0,2}$ state by Ar, CO, N_2, and O_2, and we found that $k(Ar) = 2.2 \times 10(-15)$ cm^3/sec, $k(CO) = 1.5 \times 10(-11)$ cm^3/sec, $k(N_2) = 2.8 \times 10(-11)$ cm^3/sec, and $k(O_2) = 1.2 \times 10(-10)$ cm^3/sec. Inelastic collisions between metastable argon atoms, resulting in the ionization of one collision partner, were also observed and from simultaneous electron density measurements we obtained a tentative value of $5 \times 10(-10)$ cm^3/sec for the corresponding rate coefficient. The excitation of the 2nd Positive System of $N_2(C^3\Pi_u \rightarrow B^3\Pi_g)$, produced by the depopulation of metastable argon atoms by N_2, was studied in detail and the specific rate coefficient for this important process was found to have a value of $1.2 \times 10(-13)$ cm^3/sec. The collisional deactivation of

metastable $N_2(A^3\Sigma_u^+)$ molecules by CO, O_2, and Ar
was also studied, and the following rate coefficients
were obtained: $k(CO) = 1.7 \times 10(-12)$ cm^3/sec,
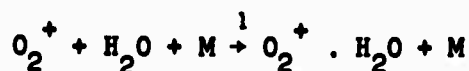$k(O_2) = 3.0 \times 10(-12)$ cm^3/sec, and $k(Ar) < 8 \times 10(-17)$
cm^3/sec.

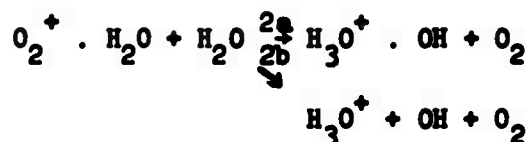6. **Ion Molecule Reactions and Excitation Processes in a Fast Flow System (F. Kaufman) (Tasks a and b).**

The studies of water cluster formation rates of NO^+ and
O_2^+ were successfully concluded. In the NO^+ work the mechanism
involves the steps

$$NO^+ + H_2O + M \xrightarrow{1} NO^+ \cdot H_2O + M$$

$$NO^+ \cdot H_2O + H_2O + M \underset{-2}{\overset{2}{\rightleftharpoons}} NO^+ \cdot 2H_2O + M$$

$$NO^+ \cdot 2H_2O + H_2O + M \underset{-3}{\overset{3}{\rightleftharpoons}} NO^+ \cdot 3H_2O + M$$

$$NO^+ \cdot 3H_2O + H_2O \xrightarrow{4} H_3O^+ \cdot 2H_2O + HONO$$

all of which were measured directly and/or by consistent computer fit
for four M, He, Ar, O_2 and N_2, i.e. a total of 21 rate constants
were obtained, since k_4 does not involve M and should therefore be
identical for all M within the error bars of the data. This was
found to be the case. A paper describing this work was submitted to
and accepted by the Journal of Chemical Physics.

The O_2^+ clustering sequence was studied in M = He, Ar,
and N_2. It consists of the steps

$$O_2^+ + H_2O + M \xrightarrow{1} O_2^+ \cdot H_2O + M$$

$$O_2^+ \cdot H_2O + H_2O \underset{2b}{\overset{2a}{\rightleftharpoons}} H_3O^+ \cdot OH + O_2$$

$$H_3O^+ + OH + O_2$$

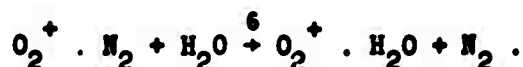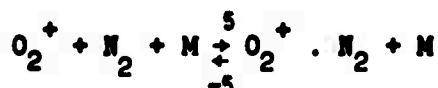with additional routes to form $O_2^+ \cdot H_2O$ in the presence of much O_2 or N_2 via

$$O_2^+ + O_2 + M \underset{-3}{\overset{3}{\rightleftharpoons}} O_4^+ + M$$

$$O_4^+ + H_2O \overset{4}{\rightarrow} O_2^+ \cdot H_2O + O_2$$

or

$$O_2^+ + N_2 + M \underset{-5}{\overset{5}{\rightleftharpoons}} O_2^+ \cdot N_2 + M$$

$$O_2^+ \cdot N_2 + H_2O \overset{6}{\rightarrow} O_2^+ \cdot H_2O + N_2 .$$
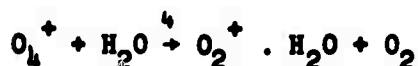
These latter steps lead to an inverse dependence of the apparent pseudo-first-order rate constant for O_2^+ decay on the concentration of added H_2O. This makes possible the indirect measurement of very slow reaction rate constants such as $k_3^{O_2}$ and $k_5^{N_2}$ which were found to be 2.5 x 10^{-30} and 8 x $10^{-31} cm^6$/sec, respectively. Consistent computer fits to the above reaction scheme were again obtained. A publication describing this work is in preparation.

7. Reactions of Metal Atoms with Ions in Magnetically Confined NO^+ Plasmas (W.L. Fite) (Tasks b and j).

Progress in this experiment has been relatively slight during the past six months since during this period the graduate student (L. M. Clendenning) was writing his thesis based on this experiment. It did become apparent during the course of his thesis writing, that the slight inhomogeneities in the magnetic confining

field introduce considerable complications into the analysis of results that lead to absolute cross sections. Rather than attempt to go through the detailed analysis, the results of which would always contain considerable uncertainties, it was decided to alter the apparatus in such a way as to reduce the magnetic field inhomogeneities and made the analysis required more simple. This work has been going on since Mr. Clendenning left.

Interestingly enough, the field inhomogeneities work in such a way as to bias the results for the ratio of ion-atom reaction to charge transfer reaction in the positive direction, i.e., detection of ion atom reaction is more sensitively done than detection of charge transfer. This implies that our previous statements that charge transfer strongly dominates over ion-atom reaction can be made even more strongly.

8. **Ion-Molecule Reactions at Elevated Temperature (M.A. Biondi) (Tasks b and j).**

The drift tube measurements of the reaction

$$U^+ + O_2 \rightarrow UO^+ + O$$
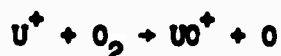
have been completed. A rate constant of 8.5×10^{-10} cm^3/sec has been found at thermal energy (300°K) decreasing to 7×10^{-10} cm^3/sec at a mean kinetic ion energy of 11 eV (in lab frame). The experimental uncertainty of these rate constants is estimated to be about $\pm$ 20%.

The corresponding reaction of U^+ with nitrogen has also been investigated. No reaction is observed to occur in the energy range from thermal to 11 eV indicating that this (endothermic) reaction is probably very slow (less than 10^{-11} cm^3/sec).

In the course of the uranium experiments it was discovered

that some neutral uranium vapor diffused from the ion source into the drift tube. While this was of little consequence for the reaction rate measurements, this effect also provided a simple way to test if a reaction of neutral uranium with O_2 would produce uranium oxide in ionized form, as suggested by some investigators. The fact that no ionized products were observed when the ion source was biased such that no ions could enter the drift cell is a strong indication that a reaction of neutral uranium with O_2 is not likely to result in ionized products. The results of the uranium experiments were presented by R. Johnsen at the 24th Gaseous Electronics Conference.

The evaporative ion source developed for uranium ions is also found to be suitable for production of aluminum ions when the uranium metal is replaced by aluminum. The reaction of aluminum ions with O_2

$$Al^+ + O_2 \rightarrow AlO^+ + O,$$
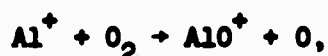
is endothermic by about 3.5 eV and cannot be expected to occur at energies available in a drift tube experiment. In agreement with this expectation, no reaction products from Al^+ were found when O_2 was admitted to the drift cell.

A recurring problem in interpreting drift tube data is that of specifying the drifting ions' velocity distribution. Without this knowledge the conversion of the measured rate constants to the more basic reaction cross sections is not possible. Since very little progress has been made in the theory of ion energy distributions in the last twenty years (following G. H. Wannier's contribution) we have decided to investigate the problem experimentally. To study the feasibility of employing a retarding potential technique, we have placed

a fine grid between the drift tube's exit orifice and the mass spectrometer and have taken a number of retarding potential curves at various values of E/p and for a number of ions with different masses (He^+, O^+, O_2^+ , and Xe^+). The results are in qualitative accord with our expectations. Gross features such as the shift in the mean energy and the increasing width of the distributions with increasing E/p can be read easily from the retarding potential curves. However, a more careful design of the retarding electrodes to avoid problems with contact potentials will be needed before this technique can be used to provide quantitative data on ion energy distributions. A means of experimentally determining velocity distributions should be of particularly great value in cases that are theoretically difficult to treat such as the drift of molecular ions in molecular gases, including the effect of inelastic collisions and related effects at very high values of E/p.

9. **Afterglow Studies of the Population of Excited Atomic and Molecular States by Vibrational Energy Transfer (E. C. Zipf) (Task d).**

Our efforts in this area have been directed into two channels: (1) Measurements of the absolute cross sections for the excitation numerous airglow and auroral emission features due to electron impact on vibrationally excited O_2 and N_2. These experiments are important in our auroral work and central to the magnetic-cusp rocket experiments (see item 14) that we will launch from Greenland. (2) We have been studying the process

$$(O_2^+)^* + O_2 \rightarrow O_2(^1\Delta) + O_2^+$$
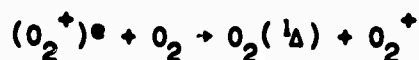
which has been proposed by Walker to explain the anomalous excitation of the $^1\Delta$ state in the auroral zone and we have obtained preliminary

evidence which supports Walker's contention that this process proceeds very rapidly ($k \sim 10^{-10}$ cm^3/sec).

10. <u>Time of Flight Experiments (E.C. Zipf) (Tasks b and d).</u>

We have continued to investigate the properties of metastable atoms and molecules and Rydberg States using translational-energy spectroscopy. These studies lead to cross section values for the basic collision processes, to the identification and location (in absolute energy as a function of the internuclear separation) of hitherto unknown molecular states, to the evaluation of radiative lifetimes, to the determination of the Auger γ-coefficient for a variety of detector surfaces (at room and elevated temperature), and to the measurement of quenching coefficients for excited states at relative impact velocities (effective temperatures) not observable in conventional many-body experiments. The latter studies are particularly interesting in the light of our in situ auroral studies. Some of our current results and their implications are summarized below:

(a) Translational Spectroscopy of Fast Metastable Fragments Produced by Electron Impact Dissociation of Atmospheric Gases. Atmospheric gases (O_2, N_2, CO, CO_2) have been bombarded by a pulsed electron beam in the 0 - 300 eV energy range and the resulting metastable fragments were detected by means of Auger ejection of secondary electrons from a metal surface in a time of flight experiment. The velocities of the dissociatively excited fragments were found to be non-thermal, with some fragments having as much as 10 eV in kinetic energy. Cross sections for the production

of slow (0.1 - 0.3 eV) fragments rapidly reached their maximum values in the 20 - 30 eV region and fell off slowly out to 300 eV whereas the cross sections for the production of fast (1 - 10 eV) fragments rose steadily from threshold to a peak around 100 eV and then fell off. These cross sections are large and imply that the presence of fast excited atoms must be taken into account in the upper atmosphere, particularly under auroral conditions where dissociative excitation plays a major role.

B. Ground Based Observations, Rocket and Satellite Measurements, and Aeronomy Calculations.

11. Optical Interferometer Studies of Barium Releases (M.A. Biondi) (Task g).

The observations of neutral barium spectral line profiles and intensities obtained in Alaska in 1969 and in Florida in 1971 yield information on the initial photoionization history of sunlit barium clouds. During the report period, a fairly simple computer program dealing with the time history of ten "species" - 8 states of neutral barium, the barium ion (electron), and barium oxide - has been developed which includes relevant populating and depopulating mechanisms for each of the "species". Radiation transport effects are neglected in this approximation. The qualitative features of some of our interferometer observations of the neutral barium behavior are reproduced when values for the relevant atomic collision rates, such as those postulated by G. Best, are used. The computer code appears useful for fixing allowable values for some of the key reaction rates.

12. Optical Photometer Studies of Nightglow Ionospheric Modifications. (M. A. Biondi) (Task g).

Using our observations of the λ6300 intensity transients

induced in the F-region of the ionosphere by the turning on and off
of a 1.6 Mw ground-based transmitter we have been able to determine
the in-situ lifetime of the $O(^1D)$ atoms as a function of altitude
over the range 225-300 km. The natural lifetime (~110 sec) of the
$O(^1D)$ state is reduced by N_2 quenching at these altitudes. Using
a model atmosphere for the N_2 density, we obtain a value for the
quenching coefficient, $k_{quench} \simeq (5 \pm 2) \times 10^{-11}$ cm^3/sec, independent
of altitude. This value is in excellent agreement with laboratory
values.

13. **Measurement of the Ionized and Neutral Constituents of the Atmosphere
    (T.M. Donahue and E. C. Zipf) (Task h).**

We continue with our analysis of two highly successful
sounding rocket studies of the transient ionosphere. The instrumentation
on board both vehicles included a quadrupole mass spectrometer that
measured the local ion and neutral composition of the upper atmosphere,
two hemispherical analyzers for measuring the photoelectron energy
distribution in the dawn and twilight ionosphere, a cylindrical probe
for electron temperature and density measurements, and a planar total
positive ion probe. These particle experiments were complemented by
a 1/4-meter Ebert monochromator that scanned the VUV dayglow spectrum
from 1150$\overset{o}{A}$ to 1500$\overset{o}{A}$ and six filtered photometers that measured the
overhead intensity of a variety of airglow features.

The dawn experiment (Aerobee 170 rocket 13.46 UA) was
particularly interesting because it took place during a major solar
flare and revealed the presence of substantial concentrations of
O^{++} ions in the F region. This ion is not a normal F region constituent,
although it has been observed occasionally by high-altitude satellites.
Our data suggest that heavy particle bombardment may be the source

of this ion.

By contrast our twilight experiment (Aerobee 350 rocket
17.09 UA), which carried a payload weighing nearly 700 lbs. to
350 km, was performed under very quiet conditions. All instruments
on board worked to perfection and we are studying these results
now.

Our analytic activities are balanced by the intensive
preparations for our return to Fort Churchill to study the aurora
and to attempt to verify our earlier NO observation. Two rockets
are being prepared for this task: an Aerobee 150 and a Nike-Apache.
Both rockets will carry a dual mode mass spectrometer equipped with
complementary cylindrical and planar probes. The Aerobee payload
will also include a liquid nitrogen cooled 1/4-meter monochromator
for infra-red out to 5 microns. The normal complement of visible VUV in-
struments that we have flown in the past are an important part of
both payloads.

During this same time window we are also preparing a new
payload that will be launched next summer from Wallops Island, Va.
on board a Javelin rocket. We anticipate a minimum peak altitude
of 800 km. This experiment will provide the first test of a new
type of optical mass spectrometer which we have developed as the re-
sult of our laboratory experiments (item 1b).

We have also embarked on a new series of rocket exper-
iments that will be launched from Greenland in collaboration with
the Danish Space Agency to study the unusual atmospheric conditions
that occur in the region of the earth's magnetic cusp. This is a
natural ex ension of our auroral and disturbed ionosphere work and

ties in very well with our laboratory studies of hot atom chemistry
(item 9 and 10).

14. **Distribution of Gases in the Mesosphere (T.M. Donahue and E.C. Zipf)
(Task f).**

Our analysis of OGO-6 photometer data continues. A paper
describing OI λ5577 measurements is being prepared and will be
submitted for publication shortly. The data relating to the
excitation of sodium D lines and the noctilucient clouds is being
analyzed and reviewed.

Plans for an elaborate mesospheric rocket experiment which
would measure the concentration of N_2, O_2, N, O, NO, OH, $O_2(^1\Delta)$,
$O_2(^1\Sigma)$, H_2O and CO_2 at D region altitudes have been finalized and
portions of the payload constructed.

C. **Theoretical Studies**

15. **Semi-Empirical Methods for Estimating Reaction Rates (E. Gerjuoy and
J.N. Bardsley) (Task e).**

(a) Our calculations of charged particle-neutral atom
collision cross sections using the Glauber approximation continue.
The papers by Thomas and Franco, and by Thomas and Gerjuoy, mentioned
in our last technical report as having been submitted for publication,
now have appeared. In addition, we have completed some rather de-
tailed calculations on the polarization of the radiation following
electron excitation as computed in the Glauber approximation. A paper
on this subject, whose initiation and motivation was explained in
our last technical report, has been submitted for publication. Since
our last technical report we also have published (in a Letter to the
Editor by Thomas, Sheorey and Gerjuoy) careful comparisons of angular
distributions and total cross sections for electron-hydrogen collisions

computed in both the Glauber and Vainshtein approximations; the
Vainshtein approximation has been favored by several groups, including
an atomic collision group in Moscow, who developed the approximation.
It was found that for integrated (over angle) elastic or inelastic
cross sections the Glauber approximation is at least as good as any
of the many (there are at least six) versions of the Vainshtein
approximation, while the Glauber differential cross sections are
markedly superior to the Vainshtein results. For computing the
polarization of the radiation following electron excitation, the Glauber,
Born and Vainshtein are about equally good, and are quite close to
the observations (by Fite and co-workers here at PASI) in the energy
range 30 eV - 700 eV. There are some discrepancies between the
computations and observations at the higher energies (500 - 700 eV)
measured, which suggest further experimental and theoretical work
on these polarizations may be instructive. As a result, a student
(D. Brocklebank), has been assigned the task of computing the angular
correlation between the photons following excitation and the outgoing
scattered electron, in the Born, Vainshtein and Glauber approximations.
It is our hope that these predictions will be sufficiently different
to provide (after comparison with hoped-for observations) a very
sensitive test of the comparative validity of the three approximations.

We are proceeding with our attempts to extend the applicability
of the Glauber approximation to the scattering of electrons and protons
by atomic systems more complicated than hydrogen. A suggested procedure
on this extension, based on the closed form Glauber amplitudes derived
and published by Gerjuoy and Thomas, has appeared (in Physical Review
Letters by V. Franco). However, we believe that Franco's procedure

still involves far too much computational effort, and we are continuing to seek a method which--for these more complicated collisions--requires not much more computer time than do the electron-hydrogen Glauber calculations.

We are pleased to report that our work on the Glauber approximation was the subject of an invited paper (by E. Gerjuoy) at the VIIth International Conference on the Physics of Electronic and Atomic Collisions) Amsterdam, July, 1971.

(b) The work on the theoretical studies of ionization and excited state populations in Ba plasmas continues, but reliable numerical results are disappointingly slow, and we are considering terminating these calculations.

(c) The quantum defect calculations by V.B. Sheorey, whose submission for publication was mentioned in our last Technical Summary Report, has appeared.

(d) A thorough review of the theory of rotational excitation of homonuclear diatomic molecules by slow electrons (by E. Gerjuoy with D. Golden, Neal Lane and A. Temkin) has been completed and accepted for publication by the Reviews of Modern Physics.

(e) Our studies of the effects of potential barriers on thermal collisions have been concentrated on the processes leading to the formation of molecules. We have shown that the presence of a high barrier does not necessarily prevent molecular formation. Indeed in some cases the reaction rate may be enhanced, as, for example, for CH formation by radiative association, and H_2 formation by three-body recombination.

(f) Our calculations on dielectronic recombination involving

electrons and highly charged ions have been completed and the results have been accepted for publication. We concluded that experimental studies of these reactions are feasible and would be useful as a check on the theory of this important recombination process.

(g) Our program for calculating cross sections for electron-atom collisions using variational techniques is being continued. In collaboration with Drs. Temkin and Bhatia of the Goddard Space Center, in Maryland, we have been studying resonant scattering of electrons by helium. This work, which is essentially completed, has involved extension of the theory of projection operators, and has given numerical results to compare with the experimental work which is at the forefront of high resolution electron collision studies. We have obtained the physical parameters of the well-known resonance at 19.3 eV. We have strong evidence that some other oscillations which have been observed in the cross section near 19.5 eV cannot be due to a resonance, and must be caused by some spurious experimental effect. We intend to study the 19.3 eV resonance further, using the complex energy method, since reliable theoretical results on this resonance are needed. This is because the resonance is used for calibrating the average energy of electron beams, and could possibly also be used for studying the energy profile of high resolution beams.

Although the standard variational techniques provide the most accurate means of calculating cross sections they do not in general provide an estimate of the error of a particular calculation. This is a serious problem in applications to large systems. We have begun an

investigation of the minimum variance technique, which not only gives an indication of the error inherent in a trial wave function, but also gives a simple prescription for choosing between trial wave functions of different types.

(h) Our studies of atom-atom and ion-atom interactions are continuing. We aim to calculate the cross sections for charge transfer and electronic excitation in Li^+-Li collisions, and have obtained the potential curves and interaction matrix elements needed in this calculation. We are now studying the particle trajectories and will then solve the coupled differential equations which govern the states of the atoms as they move along those trajectories.

Our computer program for applying the pseudopotential method to the calculation of interatomic potentials has been written, but it has not yet been fully tested. Calculation of electron impact cross sections for Be^+, Mg^+, Ca^+ and Ba^+ will soon be initiated by this technique, and a graduate student is being trained to carry through this project.

II. <u>Publications and Technical Presentations</u>

A. <u>Publications</u>

"Calculation of the Width of Narrow Shape Resonances", R. A. Bain and J. N. Bardsley, to be published in J. Chem. Phys. (1971).

"Dielectronic Recombination of Highly Charged Ions", R. A. Bain and J. N. Bardsley, to be published in Physics Letters (1971).

"Shape Resonances in Atom-Atom Collisions I. Radiative Association", R. A. Bain and J. N. Bardsley, submitted to J. Phys. B: Atom. Molec. Phys.

"Twilight and Nighttime Ionospheric Temperatures from Oxygen $\lambda6300$ and $\lambda5577$ Spectral Line Profiles", W.A. Feibelman, R.D. Hake, Jr., D.P. Sipler and M.A. Biondi., J. Geophys. Res., to be published.

"Planetary Exploration Accomplishments and Goals", T. M. Donahue, Rev. of Geophys. and Space Sci., 9, No. 1 (1971).

"Comments on the Excitation of the Geocoronal Hα Nightglow", T.M. Donahue, Planet. Space Sci., to be published.

"Aeronomy of CO_2 Atmospheres: A Review", T.M. Donahue, J. Atmos. Sci.

"Electron Capture and Loss in Collisions of Heavy Ions with Atomic Oxygen", W. L. Fite, H. H. Lo, L. Kurzweg, and R. T. Brackmann, to be published in Phys. Rev., October, 1971.

"Lyman-Alpha Emission Induced by the Collisions of Electrons with Molecular Hydrogen", W. L. Fite, W. E. Kauppila, P. J. O. Teubner and R. J. Girnius, J. Chem. Phys. 55, 1670-1672 (1971).

"The Atom-Molecule Reaction $D + H_2 \rightarrow HD + H$ Studied by Molecular Beams", W. L. Fite, J. Geddes and H. F. Krause, to be published.

"Excitation of a D-line Radiation in Collisions of Sodium Atoms with Internally Excited H_2, D_2 and N_2", W. L. Fite, J. Fricke and H. F. Krause, to be published.

"Mass and Phase Spectrometry of a Water Vapor Jet", W. L. Fite, J. Fricke and W. M. Jackson, submitted as a Note to J. Chem. Phys.

"Low Energy Electron-Molecule Scattering Experiments and the Theory of Rotational Excitation", E. Gerjuoy, D. Golden, N.F. Lane and A. Temkin, to be published, Rev. Mod. Phys.

"Comparisons of the Glauber and Vainshtein Approximation for Inelastic Electron-Hydrogen Scattering", E. Gerjuoy, B. K. Thomas and V. B. Sheorey, J. Phys. B: Atom. Mol. Phys. 4, L57-61 (1971).

"Use of the Glauber Approximation in Atomic Collisions. A Progress Report", E. Gerjuoy, to be published in the Proceedings of the Seventh International Conference on the Physics of Electronic and Atomic Collisions", Amsterdam, July, 1971 (North Holland Publishers).

"Glauber Calculations of Polarization of Lyman-α Resulting from e^{-}-H(1s) Collision", E. Gerjuoy, B. K. Thomas and V. B. Sheorey, submitted to J. Phys. B: Atom. Mol. Phys.

"Quantum defects for He I and Li II", V. B. Sheorey, J. Phys. B: Atom. Molec. Phys., 4, L44-47 (1971).

"Glauber Amplitudes in Charged Particle Hydrogen Atom Collisions", B. K. Thomas and E. Gerjuoy, J. Math. Phys. 12, 1567-1576 (1971).

"Elastic and Inelastic Scattering of Protons by Hydrogen Atoms", Victor Franco and B. K. Thomas, Phys. Rev. A 4, 945-954 (1971).

"Water Cluster Formation Rates of NO^{+} in He, Ar, N_2 and O_2 at $296°K$", C. J. Howard, H. W. Rundle, and F. Kaufman, J. Chem. Phys., to be published.

"Reactions of Metastable Nitrogen Atoms, C. L. Lin and F. Kaufman, J. Chem. Phys., to be published.

"Excitation of the CO Fourth Positive Band System by Electron Impact on Carbon Monoxide and Carbon Dioxide", M.J. Mumma, E.J. Stone and E.C. Zipf, J. Chem. Phys. $\underline{54}$, No. 6, 2627 (1971).

"Deactivation of $N_2 A^3\Sigma_u^+$ Molecules in the Aurora", T.M. Donahue, E. C. Zipf, and D. E. Shemansky, Trans. AGU, $\underline{52}$, 309 (1971).

"Differential Electron Flux as Determined by Auroral Observations of the N_2 Positive and N_2^+ Systems", D.E. Shemansky, T.M. Donahue, and E.C. Zipf, Trans. AGU, $\underline{52}$, 305 (1971).

"Excitation of the OI(^{3}S) and OI(^{5}S) States by Electron Impact on O and O_2 in the Aurora", E. C. Zipf, E.J. Stone, M. J. Mumma, W.C. Wells and W. L. Borst, Dayglow and EEUV, Trans. AGU, $\underline{52}$, 308 (1971).

"Deactivation of $N_2 A^3\Sigma_u^+$ Molecules in the Aurora", D. E. Shemansky, E. C. Zipf, and T. M. Donahue, Planetary Space Sci., in press, (1971).

"Excitation of the OI(^{3}S) and NI(^{4}P) Resonance States by Electron Impact on O and N", E.J. Stone and E.C. Zipf, Phys. Rev. A $\underline{4}$, 610 (1971).

"Non-Thermal Rotational Population of the CO(A$^1\Pi$) State Produced by Dissociative Excitation of CO_2 by Electron Impact", M.J. Mumma, E.J. Stone and E.C. Zipf, Proceedings of the Seventh International Conference on the Physics of Electronic and Atomic Collisions, p. 858 North Holland Publishing Company, Amsterdam, (1971).

"Production of Energetic Long-Lived High-Rydberg States of Atomic Nitrogen by Electron Impact Dissociation of N_2", W.C. Wells, W.L. Borst and E.C. Zipf, Proceedings of the Seventh International Conference on the Physics of Electronic and Atomic Collisions, North Holland Publishing Company, p. 576, Amsterdam (1971).

"Excitation of the Werner Bands of H_2 by Electron Impact", E.J. Stone and E.C. Zipf, submitted to the Physical Review (1971).

"Electron-Impact Excitation of Nitric Oxide", E. J. Stone and

E. C. Zipf, submitted to J. Chem. Phys. (1971).

"The Auroral Intensity Ratio of OI(6300Å) and OI(5577Å)",

T. D. Parkinson and E. C. Zipf, Planet. Space Sci., 19, 267 (1971).

B. **Technical Presentations**

"Resonant Scattering in Atomic Physics", J.N. Bardsley, Seminar talk

at the University of Connecticut, May 13, 1971.

"Atomic Collision Studies of Relevance to Planetary Atmospheres

and Inter-Stellar Space", J.N. Bardsley, Seminar talk at Harvard

College Observatory, May 14, 1971.

"Resonant States: Their Calculation and Significance", J.N. Bardsley

and R. A. Bain, paper at the Seventh International Conference on the

Physics of Electronic and Atomic Collisions (ICPEAC), Amsterdam,

July 30, 1971.

"Recombination of Electrons with Positive Ions of the $H_3O^+ \cdot (H_2O)_n$

Series", invited paper presented by R. Johnsen at the COSPAR Sym-

posium on the D and E Regions of the Ionosphere, Urbana, Illinois.

"Positive Ion Chemistry of the D and E Regions", review paper

presented by T. M. Donahue at the Symposium on D and E Region Ion

Chemistry, University of Illinois, July 6-8, 1971.

"Ionosphere, D and E Region", T. M. Donahue, invited paper at the

IUGG General Assembly, 1971, Seattle, June 18-21.

"The Temperature Dependence of Dissociative Ionization of CO_2",

W. L. Fite, invited paper at the Seventh International Conference

on the Physics of Electronic and Atomic Collisions, Amsterdam, 1971.

"Reactive Scattering of Ba by O_2 in a Crossed Beam Experiment",

W. L. Fite, Seventh International Conference on the Physics of

Electronic and Atomic Collisions, Amsterdam, 1971.

"Thermal Energy Reactions between NO^+ Ions and Metal Atoms",
W. L. Fite, invited paper at the DASA High Altitude Nuclear
Effects Symposium, Stanford Research Institute, September, 1971.

"Applications of Glauber Theory to Atomic Collisions", E. Gerjuoy,
Seminar, Louisiana State University, May 11, 1971.

"Applications of Glauber Theory to Atomic Collisions", E. Gerjuoy,
Seminar, Sandia Laboratories, Albuquerque, N. Mexico, May 13, 1971.

"Applications of Glauber Theory to Atomic Collisions", E. Gerjuoy,
Seminar, University of California, San Diego, California, May 14,
1971.

"Applications of Glauber Theory to Atomic Collisions", E. Gerjuoy,
Seminar, University of California, Berkeley, California, May 17, 1971.

"Applications of Glauber Theory to Atomic Collisions", E. Gerjuoy,
Seminar, Indiana University, Bloomington, Indiana, May 20, 1971.

"Use of the Glauber Approximation in Atomic Collisions. A Progres
Report", E. Gerjuoy, invited paper, Seventh International Conference
on the Physics of Electronic and Atomic Collisions, Amsterdam,
July, 1971.

"Gas Phase Ion-Molecule Reactions Involving Water", F. Kaufman,
Colloquium, National Bureau of Standards, Gaithersburg, Md.,
April 8, 1971.

"NO_2 Fluorescence and $0 + NO$ Chemiluminescence", F. Kaufman,
Seminar, Georgetown University, Washington, D.C., April 8, 1971.

"Gas Phase Hydrogen Atom Recombination", F. Kaufman, Seminar,
Physical and Inorganic Group, American Chemical Society, Pittsburgh,
Pa., May 19, 1971.

"Production of Energetic Long-Lived High-Rydberg States of Atomic
Nitrogen by Electron Impact Dissociation of N_2', W. C. Wells,
W. L. Borst and E. C. Zipf, Proceedings of the Seventh International
Conference on the Physics of Electronic and Atomic Collisions,
North Holland Publishing Co. (Amsterdam, 1971) p. 576.

"Non-Thermal Rotational Population of the $CO(A^1\Pi)$ State Produced
by Dissociative Excitation of CO_2 by Electron Impact", Proceedings
of the Seventh International Conference on the Physics of Electronic
and Atomic Collisions, North Holland Co. (Amsterdam, 1971) p. 858.

C. Other Activities

J.N. Bardsley and B. R. Junker have continued the collaboration
with the Goddard Space Center's group for Theoretical Studies,
and have made several visits to Washington for consultations.

M.A. Biondi participated in Secede Summer Study at Albuquerque,
N.M. in July, 1971.

M.A. Biondi participated in the Ivory Coral Technical Planning
Meeting at Albuquerque, N.M. in August, 1971.

M.A. Biondi participated as a member, Advisory Committee on Physics
of the National Science Foundation in April, 1971.

T.M. Donahue, Trustee, Upper Atmosphere Research Corp.

T.M. Donahue participated in the Outer Planets Study at Woods
Hole, Mass., August 1971.

T.M. Donahue, Member, Science Steering Group for Outer Planets
Mission.

T.M. Donahue, Member, Advisory Panel, for Atmospheric Sciences,
Division of Environmental Sciences, National Science Foundation.

W.L. Fite is co-authoring a chapter of the DASA Reaction Rate
Handbook entitled "High Energy Heavy Particle Collisions",
with A. W. Ali and J. Greene.

W.L. Fite attended meeting of Research Advisory Committee for Office
of Advanced Research and Technology at NASA.

F. Kaufman was invited to attend an AROD Review "Gaseous Interactions
and Plasma Physics", at El Paso, Texas on April 21 and 22, 1971
and chaired one of its technical sessions.

F. Kaufman was outside examiner at the Ph.D. thesis examination of
Mr. George Spindler at York University, Toronto, on May 3, 1971.

F. Kaufman attended a technical meeting on ultraviolet emission
at the Institute for Defense Analyses on July 27, 1971.

F. Kaufman was an invited member of the $\underline{ad}$ $\underline{hoc}$ Panel on the (NO_x)-Ozone
Problem of the National Academy of Sciences on July 29, 1971.

F. Kaufman attended the DNA High Altitude Nuclear Effects Symposium
at the Stanford Research Institute on August 10-12, 1971.

F. Kaufman was invited to attend the General Motors Symposium on
Emissions from Continuous Combustion Systems at Warren, Michigan
on September 27 and 28, 1971, and to be the discussor of one of its
papers.

F. Kaufman attended meetings of the Executive Committee of the Pittsburgh
Section of the American Chemical Society on June 28 and September 8,
1971.

III. Visiting Scientists

Dr. David Spence, Argonne National Laboratory

Professor Ugo Fano, University of Chicago

Dr. R. Schoen, National Science Foundation

Professor Dr. J. Kistemaker, FOM Laboratory for Atomic and Molecular Physics, Amsterdam.

Dr. M. F. R. Mulcahy, CSIRO, Chatswood, N.S.W., Australia, September 3, 1971.

Dr. Robert Schaeffer, Johns Hopkins University.

IV. <u>Degrees Awarded</u>

D.P. Sipler, Ph.D., September, 1971.

B. Guenther, Ph.D., September, 1971.

R. Nieman, Ph.D., September, 1971.

L.M. Clendenning, Ph.D., August, 1971. (Subject to revisions in thesis).

E.J. Stone, Ph.D., June, 1971.

Senior Investigator	Est. Funds Expended and Committed (Thousands)
J. N. Bardsley	22.1
M. A. Biondi	278.8
T. M. Donahue	254.0
W. L. Fite	262.2
E. Gerjuoy	253.4
F. Kaufman	264.6
E. Zipf	260.4
Total Expended and Committed	1,595.5
Available Funds	1,649.9
Estimated Remaining Funds as of 10/1/71	54.4

University Accounting of Funds

Expended as of 9/30/71	1,586.9
Available Funds	1,649.9
Remaining Funds as of 10/1/71	63.0